IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application	:	John Wilhelm Geus, et al.
Application No.	:	09/764,001
Filed	:	January 17, 2001
For	:	CATALYST AND METHOD FOR THE SELECTIVE OXIDATION OF SULFUR COMPOUNDS TO ELEMENTAL SULFUR
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Group Art Unit: 1754

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DECLARATION OF JOHN W. GEUS

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re Application of : **John W. Geus et al.**
Application No.: 09/764,001 (Continuation of Serial No. 09/142,309)
For: **CATALYST AND METHOD FOR THE SELECTIVE OXIDATION OF SULFUR COMPOUNDS TO ELEMENTAL SULFUR**
Filed: **January 17, 2001** 'Group Art Unit: 1754

DECLARATION of John W. Geus

I, John Wilhelm Geus, declare as follows:

1. I am a citizen of The Netherlands, presently residing at Gezichtslaan 100, 3723 GJ Bilthoven, The Netherlands.

2. I am Professor Emeritus of Inorganic Chemistry at Utrecht University in Utrecht, The Netherlands. I have authored and co-authored about 300 papers and am an inventor or co-inventor for about 90 patents, in the fields of catalyst production, catalytic processes, and catalytic oxidation, particularly oxidation of sulfur compounds. Presently, I am active as a consultant to a number of different chemical companies.

3. I have read the communications that have been exchanged in the prosecution of the U.S. Patent Application No. 09/142,309, the parent of the present application. More in particular, I understand that the examiner has objected, in the parent application, to the claim wording 'atomically mixed' as being indefinite in terms of adequately describing the mixed iron/zinc oxide catalyst of the present invention. I respectfully disagree, and declare that the "*atomically mixed oxide having atomically mixed iron ions and zinc ions in an oxide lattice*" language of the present claims accurately and precisely describes the mixed oxide catalysts of the invention to one of ordinary skill in the field of catalytic oxidation, particularly oxidation of sulfur compounds. This language also identifies the feature contributing to the present catalyst's improved performance. One of ordinary skill would understand that an "atomically mixed oxide" catalyst of the invention refers to one having atomically mixed metal ions – i.e., iron and zinc ions, as claimed – in an oxidic lattice, and that the atomic mixing of the iron and zinc ions could be established by examining the Mössbauer spectra of the catalyst, as taught at page 15, lines 7-25 of the specification. Specifically, the ordinarily skilled artisan would realize, based on these teachings, taken in view of the art known at the priority date of the present application, that an atomically mixed iron/zinc oxide catalyst of the invention would have a Mössbauer spectrum like that of zinc ferrite ($ZnFe_2O_4$), as shown in Fig. 3(a)-(c) of the specification.

4. The meaning of an 'atomically mixed' iron/zinc oxide catalyst may be better understood by a more detailed explanation of the problem solved by the catalyst of the invention, as follows.

5. The present invention is directed at meeting the increasingly stringent requirements for reducing sulfur dioxide emissions, by removing sulfur compounds (sometimes referred to as "sulfur") as much as possible from gas flows emitted into the atmosphere. Generally, sulfur is present in gas flows as hydrogen sulfide, together with small amounts of carbon oxysulfide and carbon disulfide. The sulfur is removed by reaction to solid or liquid elemental sulfur, which can be readily separated from the gas flow, by such processes as a "Claus process". A conventional Claus process oxidizes one third of the hydrogen sulfide to sulfur dioxide and reacts the sulfur dioxide with the remaining hydrogen sulfide to produce elemental sulfur and water. A suitable catalyst, such as titanium dioxide, is often used in the Claus process to accelerate the reaction of carbon oxysulfide and carbon disulfide with water to form carbon dioxide and hydrogen sulfide, while the resulting hydrogen sulfide reacts with the sulfur dioxide to form elemental sulfur and water.

6. Due to the position of the thermodynamic equilibrium, the reaction of sulfur dioxide with hydrogen sulfide to elemental sulfur and water does not proceed completely, when performed at temperatures at which sulfur does not condense in the catalyst and, thus, does not plug the catalyst. As a result, the sulfur recovery in conventional Claus plants is typically 96-97%. Therefore, the tail gas from a Claus plant emitted after incineration of the remaining hydrogen sulfide contains a certain, undesirable amount of sulfur dioxide, some of which is a product of residual hydrogen sulfide in the tail gas being oxidized into sulfur dioxide.

7. To increase sulfur recovery from processed gases (and thus to decrease sulfur dioxide emissions), special processes have been developed to deal with the residual hydrogen sulfide remaining in the tail gas, such as the SuperClaus^{TM} process. The SuperClaus^{TM} process increases sulfur recovery by selectively oxidizing the residual hydrogen sulfide in the tail gas into elemental sulfur. At the same time, sulfur recovery can be increased further by suppressing, as much as possible, further oxidation of the resulting elemental sulfur into sulfur dioxide. Therefore, much effort has focused on developing oxidation catalysts (advantageously, supported catalysts) that exhibit a high selectivity toward elemental sulfur and little or no activity for oxidation of elemental sulfur into sulfur dioxide. In view of the large amounts of hydrogen sulfide being processed in Claus installations, even a modest percentage increase in elemental sulfur recovery significantly diminishes overall sulfur dioxide emission levels. (For example, increasing sulfur recovery from 99.2% to 99.4%, leads to a 25% reduction in sulfur dioxide emissions.)

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8. The extensive research of my co-inventor and myself had previously indicated that iron oxide serves as a catalyst with excellent selectivity for the oxidation of hydrogen sulfide into elemental sulfur, with the iron oxide reacting partially or completely to form iron sulfate. The catalytic reaction is possible because the iron ions within the iron oxide or the iron sulfate are continuously changing their valence between two and three, under the conditions of the SuperClaus^{TM} process, which is selective for oxidation of hydrogen sulfide to elemental sulfur.

9. Molecular oxygen oxidizes the iron ions to iron(III), while hydrogen sulfide reduces the iron ions to iron(II). We have also found that further oxidation of the elemental sulfur into sulfur dioxide occurs mainly when most of the hydrogen sulfide has reacted to become elemental sulfur. The density of oxygen atoms active in the oxidation, which are adsorbed on the surface of the iron oxide/iron sulfate, appears to increase when the hydrogen sulfide has almost completely converted to elemental sulfur. In developing the present invention, we reasoned that 'dilution' of the iron ions in the catalyst, which adsorb the oxygen atoms from molecular oxygen, could limit the amount of oxygen available for oxidizing the elemental sulfur further into sulfur dioxide (since oxidation of elemental sulfur involves two oxygen atoms per sulfur atom). (See also, page 5, lines 19-21 of the specification).

10. We conceived the idea of diluting the catalyst's active sites, i.e., the valence-changeable iron ion, with inactive metal ions that do not change their valence during the selective oxidation of hydrogen sulfide. Specifically, we determined that the iron ions in the surface of the catalyst could be surrounded by inactive metal ions, e.g., zinc ions, which in turn should be surrounded by iron ions. We found that when the surface of the catalyst contains patches of active iron ions and patches of inactive metal ions, a lower activity of the catalyst will result, but without higher selectivity for the oxidation leading to elemental sulfur. Also, at the borders of significant patches of iron ions in an iron oxide-containing catalyst, the density of active oxygen tends to be elevated, which promotes oxidation of elemental sulfur to sulfur dioxide.

11. Thus the present invention provides a supported, atomically mixed iron/zinc oxide catalyst, in which individual, active iron ions of the catalytically active material (especially at its surface), are diluted or surrounded by inert zinc ions. This dilution effect significantly raises the selectivity of the catalytic oxidation toward elemental sulfur and reduces the oxidation reaction toward sulfur dioxide. The present catalyst is especially useful at high levels of

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conversion of hydrogen sulfide, providing appreciably lower oxidation of elemental sulfur to sulfur dioxide.

12.   I declare that the wording, in the present specification and claims, of "*a catalytically active material comprising atomically mixed iron and zinc ions in an oxidic lattice*" (claim 1), would indicate to one of ordinary skill in the art that the claimed catalyst's active iron ions and inactive zinc ions are atomically mixed together in the same, crystallographic or oxidic lattice, such that even within a volume of the solid catalyst down to the size of about five constituting metal ions, the chemical composition does not deviate from that of the bulk composition. The ordinarily skilled artisan would understand that the claimed catalyst excludes, by definition, any mixed oxide catalyst containing discrete patches of iron ions alone (which would destroy the higher selectivity otherwise exhibited by the atomically mixed oxide of the present invention). That same artisan also would understand that the claimed, atomically mixed oxide catalyst also excludes any mixed oxide catalyst containing two different metal ions present within different crystallographic lattices, as well as any mixed oxide catalyst that has segregated into two solid phases exhibiting the same crystallographic lattice, but of slightly different dimensions and different chemical compositions.

13.   It is important to establish that a catalyst of the present invention has atomically mixed iron and zinc ions, i.e., in a spinel lattice. Complete, atomic mixing of zinc and iron ions in a spinel lattice, such as when they form zinc ferrites of the formula $ZnFe_2O_4$, can be indicated by the paramagnetism of zinc ferrites of higher zinc contents, up to a content corresponding to $Zn_{0.4}Fe(II)_{0.6}Fe(III)_2O_4$. However, supported catalysts frequently have badly crystallized solids, whose magnetic measurements or neutron scattering measurements often provide inconclusive results. As well, as discussed in our specification, X-ray diffraction analysis cannot be used to establish atomic mixing in supported catalysts, in which the catalytically active components are usually present as finely divided particles – often only about 1 nm in size – on the surface of an inert support. For such small particles, X-ray diffraction analysis cannot discern a mixed oxide catalyst containing two or ore, atomically mixed metal ions, such as the atomically mixed iron/zinc oxide catalyst of the invention (as opposed to a mixed oxide catalyst containing discrete particles of iron oxide unmixed with zinc oxide, or a mixed oxide catalyst having two solid phases of the same crystallographic lattice, but of slightly different dimensions).

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14. As mentioned previously, and as taught in the specification, Mössbauer spectroscopy is useful to establish the presence of atomic mixing of metal ions in an oxidic lattice, as this technique is more sensitive to the local environment of individual iron atoms. That is, this technique unambiguously indicates whether iron ions in a solid are surrounded by other iron ions or by different metal ions (i.e., whether they are atomically mixed with zinc ions), which is exactly what we want to establish. Specifically, as would be understood by one of ordinary skill in the field of the invention, the properties of Mössbauer spectra that characterize the atomically mixed iron-zinc oxide catalyst of the invention, are the 'isomer shift' and the 'quadrupole splitting'.

15. The 'isomer shift' provides the following information to one of ordinary skill in the art. With Mössbauer spectroscopy, an excited nucleus is emitting a photon, which is absorbed by an iron atom in the absorber. The size of an excited nucleus is larger than that of a nucleus in the ground state. As a result, the interaction of the excited positively charged nucleus with the s-electrons around the nucleus is larger than that with the nucleus in the ground state. The different interaction of the s-electrons with nuclei in the excited and the ground state leads to absorption at a different energy. The energy at which absorption of the emitted radiation proceeds, therefore measures the density of s-electrons around the absorbing nucleus and, hence, indicates the valence of the absorbing atoms. The shift in energy at which absorption is observed as compared to the shift theoretically calculated for a single nucleus not surrounded by s-electrons is known as the 'isomer shift'. The name 'isomer' reflects the difference in size of a nucleus of an identical mass.

16. The second property of Mössbauer spectra used to determine atomic mixing, is 'quadrupole splitting'. The nucleus of iron in the ground state has a spherical charge distribution and thus no quadrupole moment. Excited to the 14.4 keV level employed for iron in Mössbauer spectroscopy the nucleus has the shape of an ellipsoide and, hence, exhibits an electrical quadrupole moment. As a result the nucleus can orient itself in an electrical field gradient in two orientations with a slight difference in energy. Accordingly two transitions from the ground state are now possible displaying a small difference in energy. The gradient of the electric field around the iron nuclei very accurately indicates the environment of the iron ions. The quadrupole splitting as apparent in Mössbauer spectra, therefore is the experimental property of choice to assess the environment of iron nuclei on an atomic scle, as is understood by one of skill in the art.

17.   Figure 3 of the specification shows the Mössbauer spectra of four materials, including:
(a) 'bulk' zinc ferrite (a: $ZnFe_2O_4$-ref); (b) finely divided zinc ferrite prepared by thermal
decomposition of a solution of iron and zinc citrate (b: $ZnFe_2O_4$-citr); (c) an atomically
mixed iron-zinc oxide catalyst according to the invention, prepared by including initially 2 %
by weight of chloride in the catalyst during calcination (c: Fe(5)Zn(10)SiCl(2)); and (d) an
iron-zinc oxide catalyst that did not initially have chloride ions present (Fe(5)Zn(10)Si). It
can be seen clearly that the distance between the two maxima of the Mössbauer spectra,
which indicates the quadrupole splitting , is different for the different materials. Whereas the
bulk zinc ferrite samples exhibit a low quadrupole splitting, the catalyst prepared without
chloride in the impregnating solution displays a much larger quadrupole splitting. Note,
furthermore, the absence of any hyperfine splitting.

18.   As appreciated by the ordinarily skilled artisan, Mössbauer spectra can be deconvoluted
accurately into different components, providing numerical information about the isomer shift
and quadrupole splitting of the different components of the spectra, as well as about the
spectral contribution. The spectra of Figure 3 of the specification have been deconvoluted
and the results are represented in the following Table. It can be seen that the isomer shift is
almost equal in all spectra, as expected.

Catalyst sample	Isomer shift mm/sec	Quadrupole splitting mm/sec	Spectral contribution %
$ZnFe_2O_4$-ref.	0.61	0.37	100
$ZnFe_2O_4$-citr.	0.61	0.46	100
Fe(5)Zn(10)Si-Cl(2)	0.61	0.44	72
	0.60	0.85	28
(Fe(5)Zn(10)Si)	0.60	0.69	59
	0.59	1.15	41

19.   Small silica-supported particles of iron(III) oxide exhibit also an isomer shift of about 0.60
mm/sec, which is to be expected in view of the same valence, but quadrupole splittings of
0.74 and 1.25 mm/sec. The different quadrupole splittings are due to the small size of the
iron oxide particles, which results in a relatively large fraction of the iron(III) ions being at
the surface of the particles. The electrical field for iron ions situated in the surface is much
less symmetrical than that of iron atoms situated inside the iron oxide particles. The

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Mössbauer spectrum of small supported iron(III) oxide particles therefore exhibits a high and a low quadrupole splitting from the surface and interior iron ions, respectively.

19.   As the table indicates the isomer shift is the same for all catalyst samples, which demonstrates that all catalysts contain iron(III) ions. The isomer shift for the bulk $ZnFe_2O_4$ is low, viz., 0.37 mm/sec, which reflects a fairly symmetrical environment of the iron(III) ions. The $ZnFe_2O_4$-citrate sample, which has been prepared by thermal decomposition of the citrates, contains zinc ferrite particles that are smaller and much less ordered, as was apparent from the X-ray diffraction pattern. The bad ordering leads to a less symmetrical electric field around the iron(III) ions and, accordingly, to a slightly higher quadrupole splitting of 0.46 mm/sec. The quadrupole splitting of the two unsupported zinc ferrite samples is much lower than that of small silica-supported iron(III) oxide particles, which is 0.74 and 1.25 mm/sec. The data of the above table show that the catalyst prepared without chloride in the catalyst during calcination displays quadrupole splittings of 0.69 and 1.15 mm/sec, which nicely agree with the values observed for pure silica-supported iron(III) oxide. The spectra of Figure 3 of the specification, including the data of the above Table from the deconvolution of the spectra, show that the components of the spectrum of the iron-zinc oxide catalyst prepared <u>without chloride</u> in the impregnating solution are almost equal to those of the spectrum of small silica-supported iron(III) oxide particles without zinc.

20.   In contrast, the data show that a catalyst according to the invention, i.e., a supported iron-zinc oxide catalyst prepared <u>with chloride</u> in the impregnating solution (Fe(5)Zn(10)Si-Cl(2)), displays a spectrum having one component that nicely agrees with the spectrum of the badly ordered bulk zinc ferrite reference, viz., the component with the quadrupole splitting of 0.44 mm/sec. The splitting of 0.44 mm/sec is due to iron(III) ions in the interior of small iron-zinc oxide particles as can be concluded from the analogous value shown by the zinc ferrite sample prepared from the citrate solution.

21.   The other spectral component, with a quadrupole splitting of 0.85 mm/sec, can only be attributed to iron(III) ions being present in the surface of the small zinc-ferrite particles present in the catalyst. The silica-supported catalysts certainly do not contain large pure iron(III) oxide particles. For someone ordinarily skilled in the art, the absence of large pure iron oxide particles is evident from the fact that the Mössbauer spectra are not showing any hyperfine splitting, which excludes the presence of large iron(III) oxide particles containing a negligible fraction of iron(III) ions in the surface of the particles. If a significant fraction of small iron oxide particles had been present, the Mössbauer spectra should have included a

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component of a quadrupole splitting of at least 1.15 mm/sec, due to the significant fraction of iron(III) ions in the surface of the necessarily small iron(III) oxide particles. It therefore can be concluded that the Mössbauer spectra indicate quite convincingly that the catalyst prepared by our method -which includes some chloride ions in the solution used to impregnate the catalyst support and leaves the chloride within the catalyst precursor during the calcination step- contains no significantly sized particles of unmixed iron oxide. Hence, our resulting catalyst's higher selectivity towards elemental sulfur, at high conversions of hydrogen sulfide, can be attributed to the absence of any iron oxide-only clumps in the catalytically active particles of the catalyst. In other words, our catalytically active material comprises an atomically mixed oxide with atomically mixed iron *and* zinc ions in an oxidic lattice.

22.　I further declare that the ordinarily skilled artisan, upon reading our application in the light of the prior art, would have understood, at the time of filing, that it was the chloride ions of the ammonium chloride included in the impregnated solution, which helped to produce an atomically mixed iron-zinc oxide catalyst on a support, with improved selectivity. That is, based upon our application's teachings that: (i) we included ammonium chloride in the iron and zinc compounds-containing solution used to impregnate the catalyst support; (ii) we left the chloride on during calcination; and (iii) the resulting mixed oxide catalyst exhibited properties of atomic mixing of the iron and zinc ions, the ordinarily skilled artisan would have appreciated, at the claimed priority date, that the chloride must have helped to bring about the iron and zinc ions' mobility and more rapid and thorough atomic mixing during calcination. The relatively high vapor pressures or volatility of many metal chlorides, such as zinc chloride, was well known in the field, at the time of the priority date of our invention. For instance, a procedure was known from the 1950s, to make zinc-steel components as protection against corrosion, by volatizing the zinc as zinc chloride by heating a mixture of zinc oxide and ammonium chloride.

23.　The above artisan would have further appreciated, based upon our application, that transport via the gas phase as zinc chloride during calcination of a catalyst of our invention, enables us to achieve an atomically mixed zinc ferrite (which is thermodynamically stable), *without having to use very elevated temperatures* to establish a sufficiently high mobility of the metal ions in the solid particles of the active precursor. At very elevated temperatures (such as those used to make prior art mixed oxide catalysts), iron-zinc catalysts strongly sinter, resulting is a severe drop in their surface area and, hence, to a severe loss of catalytic activity. In contrast, as taught in our specification and as claimed, the supported catalysts of

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our invention provide a significant amount of surface area, of over 20 m^2/g and even over 25 m^2/g, and hence, greater catalytic activity.

24. The ordinarily skilled artisan would also have appreciated at the time of our invention, that another source of chloride ions, aside from ammonium chloride, and other sources of iron and zinc ions could be used in our method of preparing the atomically mixed oxide catalyst of our invention, as described in the claims.

25. The undersigned declares that all statements made herein of my own knowledge are true and that all statements of information and belief are supposed to be true; and further, that these statements are made with the knowledge that willful false statements so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements so made may jeopardize the validity of the document, or application, or any patent issuing thereon.

Signed this 21 day of April, 2001

By : John W. Ge~

John W. Geus, Ph.D.

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